

604. *Cryoscopic Mixtures Based on Sulphuric Acid. Part I.
Proving Experiments with Model Solutes.*

By J. A. LEISTEN and K. L. WRIGHT.

Systematic measurements of freezing point have been made on four series of sulphuric acid solutions, containing disulphuric acid and disulphate ion; disulphate ion and hydrogen sulphate ion; disulphuric acid and sulphuric acidium ion; and hydroxonium ion and sulphuric acidium ion. These measurements enable results to be interpreted when the mixtures are used as cryoscopic solvents for studying reactions in sulphuric acid. Values of the van't Hoff *i*-factor for solutes of known behaviour are particularly easy to predict when the solvents are within certain ranges of composition. This is verified for each system by comparing calculated and observed *i*-factors for the solutes benzoic acid, *o*-phenylenediamine, methyl alcohol, anisic acid, and acetic anhydride.

CREDIT for developing sulphuric acid as a cryoscopic solvent is due to Hantzsch, who used it mainly to study very weak bases.¹ The technique was revived in 1933 to find *bona fide* indicators for Hammett's acidity scale,² and again in 1950 to demonstrate the existence of the nitronium ion in nitrating mixtures,³ since when it has been used repeatedly to study solutes for which unusual behaviour in strongly acidic media is expected. Near-ideal behaviour is observed even when the solutes are ionic,⁴ and sulphuric acid is in other respects a good solvent for cryoscopy;³ but there is nevertheless a general difficulty in interpreting results. Even low *i*-factors can be ambiguous, as exemplified by the observed value of 2.0 for acetone, which is correctly explained by simple protonation [eqn. (1)], but which

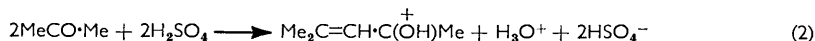
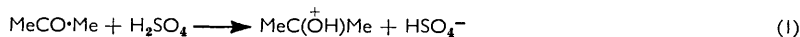
¹ Hantzsch, *Z. phys. Chem.*, 1907, **61**, 257.

² Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

³ Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.

⁴ Bass, Gillespie, and Oubridge, *J.*, 1960, 837.

on cryoscopic evidence alone can be plausibly attributed to the formation of mesityl oxide [eqn. (2)]:⁵



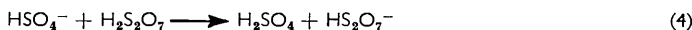
Observed *i*-factors for most solutes are higher than this, and are open to many interpretations.

This Series is concerned with four mixtures which can be used as cryoscopic solvents and which reveal to a considerable extent the nature of the particles produced when a solute is dissolved in sulphuric acid. The present Paper establishes the conditions for use of these mixtures. There have been two preliminary reports.⁶

The Sulphuric Acid-Disulphuric Acid-Disulphate System.—Since the addition of water to an oleum converts disulphuric acid to sulphuric acid

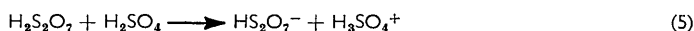


a feature of this system as a cryoscopic solvent is that water raises the freezing point instead of giving a two-fold depression as it does in sulphuric acid. A second feature is that hydrogen sulphate ions should be neutralised without changing the freezing point



because in sulphuric acid solutions, disulphuric acid behaves as a moderately strong acid,⁷ and the hydrogen sulphate ion is a strong base, analogous to the hydroxide ion in water.

There are at least two factors which make the prediction of *i*-factors in this solvent mixture uncertain. The first, acid ionisation according to the equilibrium



is minimised by the presence of disulphate ion, which is included in the mixture for this purpose. The second, which can be neither predicted nor confidently assessed, is the

TABLE 1.

Freezing points of solutions of ammonium sulphate in oleum.

Molality of $\text{H}_2\text{S}_2\text{O}_7$	Molality of * $\text{NH}_4\text{HS}_2\text{O}_7$	F. p.	Molality of $\text{H}_2\text{S}_2\text{O}_7$	Molality of * $\text{NH}_4\text{HS}_2\text{O}_7$	F. p.	Molality of $\text{H}_2\text{S}_2\text{O}_7$	Molality of * $\text{NH}_4\text{HS}_2\text{O}_7$	F. p.
0.3934	—	7.655°	0.1941	0.1428	7.782°	0.2264	—	8.833°
0.3588	0.0346	7.671	0.1587	0.1782	7.623	0.1918	0.0346	8.792
0.3233	0.0701	7.650	0.1220	0.2149	7.444	0.1567	0.0697	8.707
0.2879	0.1055	7.577	0.0869	0.2500	7.239	0.1213	0.1051	8.571
0.2510	0.1424	7.472	0.0513	0.2856	7.005	0.0858	0.1406	8.395
0.2131	0.1803	7.336	0.0159	0.3210	6.742	0.0497	0.1767	8.172
0.1768	0.2166	7.172	—	—	—	0.0145	0.2119	7.913
0.1385	0.2549	6.980	0.2814	—	8.445	—	—	—
0.1011	0.2923	6.740	0.2457	0.0357	8.424	0.1706	—	9.228
0.0614	0.3320	6.474	0.2098	0.0716	8.353	0.1375	0.0331	9.167
0.0212	0.3722	6.176	0.1732	0.1082	8.237	0.1054	0.0652	9.055
—	—	—	0.1378	0.1436	8.084	0.0734	0.0972	8.905
0.3369	—	8.053	0.1017	0.1797	7.915	0.0413	0.1293	8.715
0.3034	0.0335	8.045	0.0658	0.2156	7.695	0.0094	0.1612	8.492
0.2659	0.0710	7.989	0.0306	0.2508	7.449	—	—	—
0.2301	0.1068	7.899	0.0021	0.2793	7.239	—	—	—

* Calculated on the assumption that ammonium sulphate in oleum reacts quantitatively according to the equation:



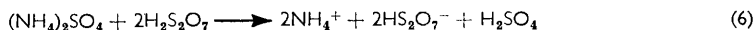
⁵ Campbell and Edward, *Canad. J. Chem.*, 1960, **38**, 2112.

⁶ Leisten, *J.*, 1961, 2191; Leisten and Walton, *Proc. Chem. Soc.*, 1963, 60.

⁷ Gillespie, *J.*, 1950, 2493.

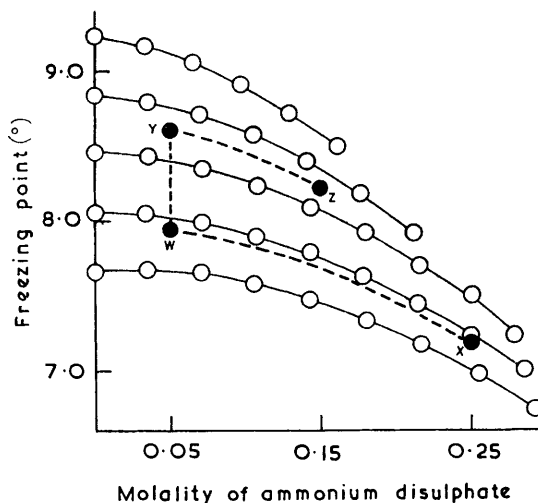
[1964] *Cryoscopic Mixtures Based on Sulphuric Acid. Part I.* 3175

presence in the system of polysulphuric acids.^{7,8} Nevertheless, the results presented in Table 1, and illustrated in the Figure, enable this solvent mixture to be used for studying the behaviour of solutes, regardless of whether or not the system behaves quantitatively according to the simple theory presented above. The Figure shows the changes of freezing point that occur as successive additions of ammonium sulphate are made to five oleums of different initial strengths, on the assumption that oleums are solutions of disulphuric acid in sulphuric acid, and that additions of ammonium sulphate produce ammonium disulphate quantitatively:



As an example of its use, suppose that a 0.2m-addition of acetone is made to the solvent represented by point W, corresponding to 0.3m-disulphuric acid and 0.05m-ammonium

Changes of freezing point on successive addition of ammonium sulphate to five oleums of different initial strengths. ○ Results from Table 1. The points W, X, Y, and Z are referred to in the text.



disulphate. If acetone merely accepts a proton, as in eqn. (1), its effect on the freezing point of this solvent should be similar to an equivalent (*i.e.*, 0.1m) addition of ammonium sulphate, and the new freezing point should be close to point X. If, however, the behaviour is as shown in eqn. (2), the water liberated would reduce the molality of disulphuric acid by 0.1, raising the freezing point to Y, while the simultaneously produced mesityl oxide should exert a lowering effect similar to that of 0.05m-ammonium sulphate, the combined effects giving a freezing point close to Z. The freezing points X and Z, 7.19° and 8.21°, respectively, can be determined by interpolations, as suggested by the broken lines in the Figure. The difference is obviously great enough to allow distinction between the two modes of behaviour. Similar predictions can be made for other solutes and other types of behaviour; non-electrolytes must be assumed to produce unit depressions of freezing point.⁹

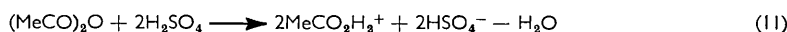
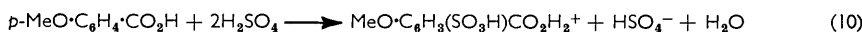
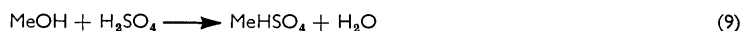
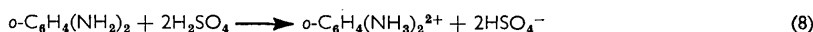
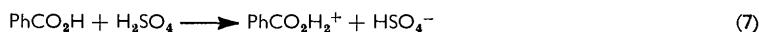
In order to show that it can be used successfully, five solutes, whose chemical behaviour in sulphuric acid is known with reasonable certainty, have been examined in the system. The behaviour of the solutes benzoic acid, *o*-phenylenediamine, methyl alcohol, anisic acid,¹⁰ and acetic anhydride,¹¹ is suitably represented for the present purpose by eqns. (7)—(11).

⁸ Dacre and Wyatt, *Trans. Faraday Soc.*, 1961, **57**, 1958.

⁹ Brayford and Wyatt, *J.*, 1955, 3453.

¹⁰ For references, see Gillespie and Leisten, *Quart. Rev.*, 1954, **8**, 40.

¹¹ Leisten, *J.*, 1955, 298.



It can be shown from the Figure that, for small additions of solute to solvent mixtures within a certain composition range, the change of freezing point should be reasonably in accord with the simple theory summarised by eqns. (3) and (4), the results, in consequence, being particularly easy to interpret and express. The results given in Table 2 were

TABLE 2.

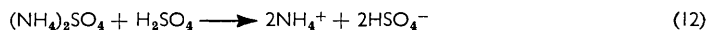
i-Factors for model solutes in sulphuric acid–disulphuric acid–disulphate mixtures.

Molality of			<i>i</i> -Factor		Molality of			<i>i</i> -Factor	
H ₂ S ₂ O ₇	NH ₄ HS ₂ O ₇	solute	(calc.)	(obs.)	H ₂ S ₂ O ₇	NH ₄ HS ₂ O ₇	solute	(calc.)	(obs.)
Benzoic acid					Anisic acid				
0.24	0.10	0.048	1.00	0.88	0.22	0.12	0.049	0.00	-0.05
0.18	0.16	0.049	„	1.12	0.18	0.16	0.050	„	+0.24
0.13	0.21	0.050	„	1.31	0.16	0.06	0.051	„	-0.07
0.16	0.07	0.049	„	0.87	0.13	0.10	0.051	„	+0.25
0.13	0.10	0.049	„	1.08	Acetic anhydride				
<i>o</i> -Phenylenediamine					0.24	0.10	0.056	3.00	2.72
0.19	0.15	0.050	1.00	0.54	0.19	0.15	0.051	„	2.93
0.13	0.20	0.050	„	0.99	0.16	0.06	0.077	„	2.87
Methyl alcohol					0.13	0.10	0.053	„	2.99
0.23	0.10	0.072	0.00	+0.02					
0.19	0.15	0.055	„	+0.14					
0.16	0.06	0.062	„	+0.01					
0.13	0.10	0.051	„	+0.13					

obtained under these conditions. The calculated *i*-factor of zero for anisic acid is the sum of +1 for the species C₆H₃(OMe)(SO₃H)CO₂H₂⁺, 0 for the hydrogen sulphate ion [see eqn. (4)], and -1 for the water molecule produced [see eqn. (3)]. The observed *i*-factors in this case are all zero, to within one quarter of a unit. The calculation of *i*-factors for the other four solutes is straightforward, and again there is satisfactory agreement with observed *i*-factors, except perhaps for one measurement where the difference is nearly half a unit.

To summarise, this system can be used as a cryoscopic solvent in either of two ways. The more convenient way is to control the conditions, and to compare observed *i*-factors with those calculated from simple theory. A suitable solvent for this purpose is one containing 0.18m-disulphuric acid and 0.10m-disulphate ion. The concentration of solute to be studied should not exceed 0.05m. In cases where several molecules of water and/or hydrogen sulphate ions are produced per molecule of solute, this procedure will lead to error, and the other method, based on the results in Table 1, and exemplified above with the solute acetone, must be used.

The Sulphuric Acid–Disulphate–Hydrogen Sulphate System.—If ammonium sulphate, in excess of the amount required by eqn. (6), is added to an oleum, the excess forms ammonium hydrogen sulphate, and an essentially different cryoscopic solvent is produced:



According to simple theory, water added to this solvent should not alter the freezing point, but hydrogen sulphate ions should produce the same depression as in sulphuric acid:



[1964] *Cryoscopic Mixtures Based on Sulphuric Acid. Part I.* 3177

The results given in Table 3 can be used graphically to distinguish between different modes of solute behaviour in a similar way to that described for the previous system, and this is the most general procedure; but, as before, it is found from the graph that over a range of conditions the simple theory should be adequate, and *i*-factors can be calculated, for comparison, with those observed. The comparison is made in Table 4 for the five model solutes, and agreement is satisfactory. A suitable mixture is one containing 0.10m-ammonium disulphate and 0.10m-ammonium sulphate.

The Sulphuric Acid-Sulphuric Acidium-Disulphuric Acid System.—Flowers, Gillespie,

TABLE 3.

Freezing points of solutions of ammonium sulphate in oleum.

Molality of * NH ₄ HS ₂ O ₇	Molality of NH ₄ HSO ₄	F. p.	Molality of * NH ₄ HS ₂ O ₇	Molality of NH ₄ HSO ₄	F. p.	Molality of * NH ₄ HS ₂ O ₇	Molality of NH ₄ HSO ₄	F. p.
0.2004	0.0440	7.704°	0.1487	0.1745	6.881°	0.1011	0.2865	6.077°
"	0.0787	7.364	"	0.2101	6.486	"	"	"
"	0.1136	7.028	"	0.2450	6.086	0.0497	0.0002	9.794
"	0.1493	6.647	"	"	"	"	0.0358	9.448
"	0.1835	6.276	0.1011	0.0342	8.862	"	0.0709	9.075
"	0.2117	5.974	"	0.0690	8.524	"	0.1059	8.694
0.1487	0.0361	8.320	"	0.1044	8.147	"	0.1409	8.306
"	0.0710	7.975	"	0.1396	7.767	"	0.1759	7.899
"	0.1052	7.626	"	0.1749	7.372	"	0.2105	7.499
"	0.1398	7.258	"	0.2102	6.986	"	0.2607	6.894
"	"	"	"	0.2485	6.530	"	0.3105	6.295

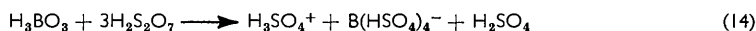
* This column also gives the molality of H₂S₂O₇ in the solvent before addition of (NH₄)₂SO₄.

TABLE 4.

i-Factors for model solutes in sulphuric acid-disulphate-hydrogen sulphate mixtures.

Molality of			<i>i</i> -Factor		Molality of			<i>i</i> -Factor	
NH ₄ HS ₂ O ₇	NH ₄ HSO ₄	solute	(calc.)	(obs.)	NH ₄ HS ₂ O ₇	NH ₄ HSO ₄	solute	(calc.)	(obs.)
Benzoic acid					Anisic acid				
0.20	0.05	0.050	2.00	1.86	0.20	0.05	0.050	2.00	1.78
0.20	0.10	0.050	"	2.01	0.20	0.10	0.050	"	1.92
0.10	0.05	0.049	"	1.88	0.10	0.05	0.050	"	1.79
0.10	0.10	0.050	"	1.95	0.10	0.10	0.049	"	2.08
					0.10	0.15	0.049	"	2.20
<i>o</i> -Phenylene diamine					Acetic anhydride				
0.20	0.10	0.049	3.00	2.70	0.20	0.05	0.048	4.00	3.71
0.10	0.05	0.050	"	2.57	0.20	0.10	0.045	"	3.71
0.10	0.10	0.050	"	2.91	0.10	0.05	0.050	"	3.68
					0.10	0.10	0.049	"	3.78
					0.10	0.15	0.051	"	3.82
Methyl alcohol									
0.20	0.05	0.052	1.00	0.98					
0.20	0.10	0.053	"	1.16					
0.10	0.05	0.045	"	0.94					
0.10	0.10	0.046	"	1.20					

and Oubridge¹² showed that the addition of boric acid to oleum produces tetra(hydrogen sulphato)boric acid, which ionises as a strong acid:



If the system contains an excess of disulphuric acid, the addition of water should remove disulphuric acid as shown by eqn. (3), and so produce a unit elevation of the freezing point. Hydrogen sulphate ions should have exactly the same effect through the neutralisation reaction



¹² Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

Subsequent studies have shown that other species may be present in these solutions,¹³ and so once again systematic measurements of freezing point have been made so that the system should be useful as a cryoscopic solvent, regardless of whether or not the simple theory holds quantitatively. The results given in Table 5 were obtained by progressively

TABLE 5.
Freezing points of solutions of boric acid and ammonium sulphate in oleum.

Molality of			F. p.	Molality of			F. p.
H ₂ S ₂ O ₇	HB(HSO ₄) ₄	NH ₄ B(HSO ₄) ₄		H ₂ S ₂ O ₇	HB(HSO ₄) ₄	NH ₄ B(HSO ₄) ₄	
0.2975	0.0973	—	7.484°	0.1045	0.0192	0.0821	8.716°
„	0.0728	0.0245	7.545	„	0.0022	0.0991	8.689
„	0.0516	0.0457	7.580				
„	0.0292	0.0681	7.609	0.1065	0.1689	—	8.001
„	0.0051	0.0922	7.621	„	0.1453	0.0236	8.052
				„	0.1222	0.0467	8.080
0.1045	0.1013	—	8.680	„	0.0985	0.0704	8.117
„	0.0804	0.0209	8.699	„	0.0745	0.0944	8.136
„	0.0587	0.0426	8.712	„	0.0512	0.1177	8.141
„	0.0365	0.0648	8.719	„	0.0272	0.1417	8.140
				„	0.0029	0.1660	8.080

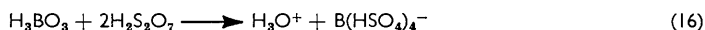
TABLE 6.

i-Factors for model solutes in sulphuric acid–sulphuric acidium–disulphuric acid mixtures.

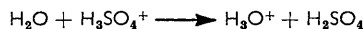
Solute	Molality of			<i>i</i> -Factor	
	H ₂ S ₂ O ₇	H ₂ SO ₄ ⁺	solute	(calc.)	(obs.)
Benzoic acid	0.10	0.072	0.051	0.00	+0.20
<i>o</i> -Phenylenediamine	0.10	0.072	0.026	-1.00	-1.08
Methyl alcohol	0.11	0.071	0.063	0.00	+0.01
Anisic acid	0.11	0.071	0.050	-1.00	-0.85
Acetic anhydride	0.10	0.072	0.024	+1.00	+1.39

neutralising, with ammonium sulphate, solutions of tetra(hydrogen sulphato)boric acid in oleum. By examining the results graphically, it can be shown that a mixture which contains 0.1m-disulphuric acid and 0.07m-sulphuric acidium ion should behave according to the theory given above, and results for the five test solutes in this mixture are given in Table 6. The agreement between calculated and observed *i*-factors is satisfactory.

The Sulphuric Acid–Sulphuric Acidium–Hydroxonium System.—If boric acid is added to oleum containing three times the molar amount of disulphuric acid, reaction occurs according to eqn. (14). If the oleum contains twice the molar amount of disulphuric acid, the reaction is:¹²



Oleums of intermediate concentration give rise to mixtures of tetra(hydrogen sulphato)boric acid and hydroxonium tetra(hydrogen sulphato)boric acid. Addition of water to such mixtures should not change the freezing point



while addition of hydrogen sulphate ion should produce unit elevations of freezing point, by reaction (15). The results given in Table 7 were obtained in a similar way to those given in Table 5, but using less concentrated oleums. These results suggest the use of a mixture containing 0.13m-sulphuric acidium ion and 0.10m-hydroxonium ion, and Table 8 shows the cryoscopic behaviour of the five solutes in this solvent.

¹³ Gillespie and Robinson, *Canad. J. Chem.*, 1962, **40**, 1009.

EXPERIMENTAL

Freezing-point measurements were made according to Treffers and Hammett,¹⁴ with certain modifications. The Beckman thermometer was replaced by a thermometer of fixed range (6—11°).¹⁵ The glass-spiral stirrer was operated by a single solenoid.⁹ Solid solutes were added to the cryoscope by means of a simple tube closed at one end and bent at an angle

TABLE 7.
Freezing points of solutions of boric acid and ammonium sulphate in oleum.

Molality of			F. p.	Molality of			F. p.
H ₃ OB(HSO ₄) ₄	HB(HSO ₄) ₄	NH ₄ B(HSO ₄) ₄		H ₃ OB(HSO ₄) ₄	HB(HSO ₄) ₄	NH ₄ B(HSO ₄) ₄	
0.0984	0.1362	—	7.711°	0.0558	0.1657	—	7.736°
"	0.1120	0.0242	7.728	"	0.1419	0.0238	7.884
"	0.0878	0.0484	7.749	"	0.1183	0.0474	7.894
"	0.0637	0.0725	7.716	"	0.0938	0.0719	7.905
"	0.0395	0.0967	7.631	"	0.0694	0.0963	7.876
				"	0.0461	0.1196	7.780
				"	0.0229	0.1428	7.611

TABLE 8.

i-Factors for model solutes in sulphuric acid–sulphuric acidium–hydroxonium mixtures.

Solute	Molality of			<i>i</i> -Factor	
	H ₃ O ⁺	H ₃ SO ₄ ⁺	solute	(calc.)	(obs.)
Benzoic acid	0.10	0.13	0.050	0.00	+0.17
<i>o</i> -Phenylenediamine	0.10	0.13	0.025	−1.00	−1.03
Methyl alcohol	0.10	0.14	0.051	+1.00	+1.16
Anisic acid	0.11	0.13	0.025	0.00	+0.23
Acetic anhydride	0.10	0.13	0.025	0.00	+0.20

of 135°. Liquid solutes were added with an "Agla" micro-syringe.¹⁶ To induce freezing of the supercooled sulphuric acid solutions, the cryoscope was temporarily removed from the air-jacket and cooled locally with solid carbon dioxide. A slightly different supercooling correction was adopted,³ and van't Hoff *i*-factors were obtained from the equation $i = \Delta\theta/6.0m$, where $\Delta\theta$ is the freezing-point depression produced by a solute of molality *m*.

The concentrations of oleums were determined from Gillespie's freezing-point data.¹⁷ All solutes were carefully purified and dried.

The following mixtures are suitable for most purposes. A solution containing 0.18m-disulphuric acid and 0.10m-disulphate ion is obtained by adding 0.66 g. of ammonium sulphate to 100 g. of oleum of f. p. 8.46°. A solution containing 0.10m-disulphate ion and 0.10m-hydrogen sulphate ion is obtained by adding 1.32 g. of ammonium sulphate to 100 g. of oleum of f. p. 9.73°. To prepare the mixture with 0.10m-disulphuric acid and 0.07m-sulphuric acidium ion, add 0.43 g. of boric acid to 100 g. of oleum of f. p. 8.24. To prepare the mixture with 0.10m-hydroxonium ion and 0.13m-sulphuric acidium ion, add 1.43 g. of boric acid to 100 g. of oleum of f. p. 6.27°.

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¹⁴ Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1708.

¹⁵ Gillespie and Leisten, *J.*, 1954, 1.

¹⁶ Duffy and Leisten, *J.*, 1960, 545.

¹⁷ Gillespie, *J.*, 1950, 2516.